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A01N 25/14**A01N 25/08**(21)Application number : **03-286991**(71)Applicant : **SHIONOGI & CO LTD**
HOKKO CHEM IND CO LTD(22)Date of filing : **07.10.1991**(72)Inventor : **UNO IKUO**
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NAGAO SHIGEYUKI**(54) AGRICULTURAL WETTABLE POWDER COMPOSITION**

(57)Abstract:

PURPOSE: To provide the subject composition composed of an agricultural active component, a surfactant and a specified carrier for reducing coagulation and precipitation of the active component as low as possible, remarkably improved in shelf life and workability in preparation and application.

CONSTITUTION: The objective composition contains (A) an agricultural active component, (B) a carrier composed of precipitated silica having ≤ 3.5 per nm² surface hydroxyl group density and (C) a surfactant (e.g. alkylarylsulfonate). As the component (A), a compound having $\leq 70^{\circ}\text{C}$ melting point, e.g. 0,0- dimethyl-0-[3-methyl-4-(methylthio)phenyl] thiophosphate is preferable from the viewpoint of preventing precipitation and coagulation. The component (B) is obtained, e.g. by heating precipitated silica prepared by the known method at 700-1000°C for 10-20min.

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CLAIMS

[Claim(s)]

[Claim 1] The hydration agricultural-chemicals constituent characterized by a surface water acid radical consistency using the sedimentation nature silica of two or less [3.5 //nm] as said support in the hydration agricultural-chemicals constituent containing an agricultural-chemicals active principle, the support which supports this agricultural-chemicals active principle, and a surfactant.

[Claim 2] The hydration agricultural-chemicals constituent according to claim 1 whose steam adsorption specific surface area of said sedimentation nature silica is 15-45m²/g.

[Claim 3] The hydration agricultural-chemicals constituent according to claim 1 or 2 whose melting point of one sort or two sorts or more of mixture of said agricultural-chemicals active principle is 70 degrees C or less.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About hydration agricultural-chemicals constituents, such as water dispersible powder, if this invention is explained further in full detail, it will control the flocking-settling nature of an agricultural-chemicals active principle as much as possible, and it relates to the hydration agricultural-chemicals constituent which made the workability at the time of the preservation stability and pharmaceutical preparation preparation, and spraying improve by leaps and bounds.

[0002]

[Description of the Prior Art] It sets to agricultural-chemicals pharmaceutical preparation, such as an insecticide, a germicide, and a herbicide, and pressure of business of the preservation stability of the agricultural-chemicals active principle in the pharmaceutical preparation concerned (agricultural-chemicals original object), the workability at the time of use, and the hydration agricultural-chemicals constituent of the water-dispersible-powder type which adds and uses water from the homogeneity of the use effectiveness (the pharmacology effectiveness) further at the time of use is carried out in recent years.

[0003] After making support for agricultural chemicals, such as clay, talc, the diatom earth, a kaolin, a bentonite, and a water silicon dioxide (a common name is carried out to a silica or white carbon), support an agricultural-chemicals active principle and usually adding a surfactant and the additive further for a stabilizing agent and its other places to this, this hydration agricultural-chemicals constituent carries out grinding mixing of this mixture with a hammer mill etc., and is manufactured.

[0004] However, it is known that the agricultural-chemicals active principle in this constituent will receive hydrolysis gradually, and the agricultural-chemicals constituent obtained by doing in this way will fall the content with time. Therefore, if it is in this hydration agricultural-chemicals constituent, it is very important practically to maintain that stability with time, and this stability maintenance or improvement is benefited for various proposals also from the former.

[0005] For example, invention about the mineral matter support for agricultural chemicals which heat-treated mineral matter, such as clay, talc, and a bentonite, with the burning temperature of 800 degrees C or more is indicated by JP,57-156402,A.

[0006] Moreover, baking composition water silicon oxide is made to support fenitrothion to JP,59-53402,A, invention about the fenitrothion water dispersible powder which controlled that the fenitrothion of a original object dissociated in the shape of an oil droplet at the time of hydration is indicated, and invention of an agricultural-chemicals constituent which makes the water silicic acid whose loss on ignition is 2 or less % of the weight come to support an agricultural-chemicals active principle is indicated by JP,1-55241,B at it.

[0007] Furthermore, the burned product and surfactant of an agricultural-chemicals original object and a wet method silica whose melting point is 70 degrees C or less are used as an indispensable component, and invention about wet piston granulation or the granularity water dispersible powder obtained by carrying out dry type granulation is indicated by JP,3-163006,A in this.

[0008]

[Problem(s) to be Solved by the Invention] Extent in these well-known invention controlling hydrolysis of an agricultural-chemicals active principle, and preventing oil droplet-like separation with the water of this agricultural-chemicals active principle etc., and it maintaining the preservation stability of an agricultural-chemicals constituent, and raising it is effective.

[0009] However, if it is in the well-known hydration agricultural-chemicals constituent to apply, the support which supported the agricultural-chemicals active principle at the time of hydration condenses with time with said agricultural-chemicals active principle, it sediments at the container pars basilaris ossis occipitalis, and bringing about various un-arranging in activity is known.

[0010] That is, the homogeneity of distribution of the agricultural-chemicals active principle in the so-called hydration agricultural-chemicals constituent like water dispersible powder is influenced to the underwater dispersibility (coherent) of the support which supported this active principle quite strongly.

[0011] As porosity fine particles as support for agricultural chemicals, the sedimentation nature silica is conventionally used widely from the high oil absorption ability as everyone knows. Many hydroxyl groups (an OH radical, silanol group) exist in the particle front face of this sedimentation nature silica, and since it is that chemical property, the silica concerned tends to start flocking settling with an agricultural-chemicals active principle etc. in water dispersible powder.

[0012] Therefore, it is requested conventionally that flocking settling of the support at the time of the hydration of this hydration agricultural-chemicals constituent and/or an agricultural-chemicals active principle with time is prevented.

[0013]

[Means for Solving the Problem and its Function] The result of having examined wholeheartedly the cause and its solution approach of said flocking settling in a hydration agricultural-chemicals constituent in order that this invention persons might meet the above-mentioned request, That the flocking-settling nature of water dispersible powder can be considerably controlled by adjusting the hydroxyl-group consistency of the sedimentation nature silica particle front face as support to a certain range A header, Furthermore, when research was repeated about the optimum density of this hydroxyl group, and the consistency of the hydroxyl group concerned was made or less [3.5 //nm] into two, the knowledge of the flocking-settling nature of said water dispersible powder being sharply improvable was carried out.

[0014] That is, according to examination of this invention persons, the surface water acid radical consistency of the sedimentation nature silica conventionally used as support of a hydration agricultural-chemicals constituent was usually about [8-10 //nm] two, and few things were also things before and behind five-piece [/nm] 2. However, when it considers as water dispersible powder by making this silica into the support for agricultural chemicals, flocking settling is carried out remarkably.

[0015] To the sedimentation nature silica the surface water acid radical consistency of whose is two or less [3.5 //nm], however, an agricultural-chemicals active principle, The hydration agricultural-chemicals constituent which especially the melting point made support a component 70 degrees C or less, and carried out mixed preparation with the surfactant When water is made to carry out suspension distribution of this, there is little flocking settling remarkably, the stable dispersibility is shown, therefore the workability of spraying and the homogeneity of an agricultural-chemicals active principle are improved, the knowledge of having the property for which it was very suitable as a hydration agricultural-chemicals constituent is carried out, and it comes to complete this invention.

[0016] Therefore, this invention offers the hydration agricultural-chemicals constituent characterized by a surface water acid radical consistency using the sedimentation nature silica of two or less [3.5 //nm] as said support in the hydration agricultural-chemicals constituent containing an agricultural-chemicals active principle, the support which supports this agricultural-chemicals active principle, and a surfactant.

[0017] in addition -- although the reason for giving the effectiveness which was excellent as mentioned above has an unknown hydration agricultural-chemicals constituent concerning this invention -- a surface-water acid-radical consistency -- the sedimentation nature silica of two or less [3.5 //nm] -- if independent, since high flocking-settling tightness does not give, it is thought that three persons of a surfactant who make water carry out suspension distribution of the silica which supports this silica, the agricultural-chemicals active principle supported by this, and this agricultural-chemicals active principle act in multiplication, and give high distributed stability.

[0018] Hereafter, if it explains in detail, the hydration agricultural-chemicals constituent of this invention comes to

contain per this invention and also an agricultural-chemicals active principle and the support which supports this, and a surfactant, at the time of use, will carry out suspension distribution and will use them for water.

[0019] Here, in this invention, the surface water acid radical consistency uses the sedimentation nature silica which is two or less [3.0 //nm] more preferably two or less [3.5 //nm] as the above-mentioned support. When a surface water acid radical consistency makes water carry out suspension distribution of the hydration agricultural-chemicals constituent which made this support an agricultural-chemicals active principle with a sedimentation nature silica with more [nm] 3.5 pieces /than 2, flocking settling increases and the purpose of this invention cannot be attained.

[0020] Although various descriptions other than the surface water acid radical consistency of the sedimentation nature silica support used for this invention are selected, it is desirable that points, such as dispersibility over water and workability at the time of pharmaceutical preparation preparation, to steam adsorption specific surface area is 15-45m²/g. Moreover, as for oil absorption, it is desirable that they are 200-350ml / 100g, and the range of mean particle diameter is usually 1-10 micrometers.

[0021] As for the sedimentation nature silica which has the above surface water acid radical consistencies, the sedimentation nature silica obtained by the usual well-known approach can be obtained, for example by heat-treating 700-1000 degrees C for 10 - 120 minutes, or carrying out silane coupling processing.

[0022] On the other hand, as an agricultural-chemicals active principle supported by the above-mentioned sedimentation nature silica, although there is especially no limit, a thing 70 degrees C or less is suitably used for the melting point of one sort or two sorts or more of mixture of an agricultural-chemicals active principle from the point of sedimentation condensation tightness, and the following are illustrated as such an agricultural-chemicals active principle.

[0023] O and O-dimethyl-O-[3-methyl-4-(methylthio) phenyl] thio phosphate (liquid)
O and O-dimethyl-O-(3-methyl-4-nitrophenyl) thio phosphate (liquid) (fenitrothion)
Dimethyl dithio phosphoryl ethyl phenylacetate (liquid)
(2-isopropyl-4-methyl pyrimidyl -6)-diethyl thio phosphate (liquid)
Dimethyl JIKARUBETOKISHI ethyl dithiophosphate (liquid)
3-phenoxy benzyl =(1RS, 3RS)-(1RS, 3RS)-3-(2 and 2-dichloro vinyl)-2 and 2-dimethyl cyclopropane carboxylate (liquid)
(RS)-alpha-cyano-3-phenoxy benzyl =(RS)-2-(4-chlorophenyl)-3-methyl BUTANO art (liquid)
O-ethyl - S and S-diphenyl dithiophosphate (liquid)
PENTA-4-enyl = N-furfuryl - N-imidazole-1-yl-carbonyl-DL-gay ARANINATO (liquid) (BEFURAZOETO)
It is the ordinary temperature of ** and is the component of a liquid.

[0024] O and O-diethyl-O- 3, 5, and 6-Tori Krol-2-pyridyl phosphorothioate (m. p.43 degree C)
O, O-dimethyl-S[5-methoxy - 1, 3, 4-thia JIAZORU-2(3H)-ONIRU-(3)-methyl] dithiophosphate (m. p.39 degree C)
O and O-diisopropyl-S-benzyl thio phosphate (m. p.23 degree C)
2-methyl-4-chloro FENIKISHICHIO acetic-acid-S-ethyl (m. p.41 degree C)
Isopropyl-N-(3-KURORU phenyl) carver mate (m. p.42 degree C)
S-1-methyl-1-phenylethyl = piperidine-1-KARUBOCHI art (m. p.39 degree C)
ECHIRUPARA nitrophenyl CHIONOBENZEN phosphonate (m. p.36 degree C)
2-secondary butylphenyl-N-methyl carver mate (m. p.32 degree C)
2-(4-ethoxy phenyl)-2-methylpropyl =3-phenoxy ZENJIRU = ether (m. p.36.4-38.0 degrees C) (etofenprox)
It is the ordinary temperature of ** and is a wax-like component.

[0025] O and O-diethyl-O-(3-oxo-- 2-phenyl-2H-pyridazine-6-IRU) phosphorothioate (m. p.55 degree C)
O and O-dimethyl-S-(N-methyl carbamoyl methyl) JIOHOSUFETO (m. p.51 degree C)
3-diethoxy phosphoryl thiomethyl-6-KURORU bends oxazolone (m. p.48 degree C)
2-methoxy-4H- a 1, 3, and 2-benzodioxo phospholine-2-sulfide (m. p.55 degree C)
(E) -4-chloro - alpha, alpha, and alpha-Tori Fluor-N -(1-imidazole-1-IRU-2-propoxy ethylidene)- Ortho toluidine (m. p.63 degree C)
N-butyl-N-ethyl - alpha, alpha, and alpha-Tori Fluor -2, 6-dinitro-para toluidine (m. p.66 degree C)
N-(1-ethyl propyl)-3, the 4-dimethyl -2, 6-dinitro aniline (m. p.58 degree C)
The component which serves as a liquid or a semisolid with the temperature at the time of pharmaceutical preparation although it is a solid-state in the ordinary temperature of **.

[0026] As a surfactant used by this invention, each surfactant usually used for a hydration agricultural-chemicals constituent can use it, for example, it can use combining one sort, such as alkylaryl sulfonates, a naphthalene sulfonic-acid formalin condensate, a ligninsulfonic acid salt, dialkyl sulfosuccinate, a polyoxyethylene-alkyl-aryl-

ether sulfate salt, polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, fatty-acid polyoxyethylene sorbitan, and sorbitan alkyl ester, or two sorts or more. In addition, in an amount, the amount of these surfactants used is good, and, generally is usually 1 - 10% of the weight of the whole constituent.

[0027] The various additives of arbitration which can blend the powder of an ammonium sulfate besides the powder of the mineral matter usually further used [attapulgit / agalmatolite, silica, silica sand, a pottery stone, a kaolin, diatomaceous earth, clay, talc, a calcium carbonate,] by the need as an extending agent, a urea, ****, a glucose, a sodium sulfate, and potassium chloride etc., in addition are used for a hydration agricultural-chemicals constituent can also be blended with the agricultural-chemicals constituent of this invention.

[0028]

[Example] Although an example and the example of a comparison are shown and this invention is concretely explained while the example of manufacture of the sedimentation nature silica support used by this invention is shown hereafter, this invention is not restricted to the following example.

[0029] The No. 3 sodium silicate of [example of manufacture] marketing is diluted for specific gravity 1.07 (55 degrees C), 5l. of this diluent is put into a reaction tank, and 300ml of 42.5% of sulfuric acids is poured into the bottom of the temperature of 92**2 degrees C in 35 minutes, agitating.

[0030] Aging is performed for after [sulfuric-acid pouring] 40 minutes. After aging adjusts pH of a reaction slurry to 4.0, cooling radiationally, then, performs filtration rinsing by the nutsche, **** a reaction by-product (sodium sulfate); and separates it.

[0031] This rinsing cake is slurred again, pH adjustment is performed, and filtration and rinsing are again performed after pH adjustment. Subsequently, sedimentation nature silica powder was obtained by desiccation and grinding.

[0032] This sedimentation nature silica 500g was put into the iron tray, this was heat-treated at 870 degrees C among the electric furnace for 1 hour, and this was made into the silica (1).

[0033] Moreover, sedimentation nature silica 500g obtained like the above was heat-treated at 900 degrees C for 0.5 hours, and this was made into the silica (2).

[0034] The description of the above-mentioned silica (1) and (2) is shown in Table 1. In addition, the description of the commercial silicas A and B is also collectively shown in Table 1.

[0035]

[Table 1]

		シリカ (1)	シリカ (2)	市販 シリカ A	市販 シリカ B
乾燥減量 (%)		0.9	1.8	6.2	1.6
pH		6.3	6.4	5.8	7.2
吸油量 (ml/100g)		226	231	236	263
平衡水分 (37 °C, 72 %) (%)		1.8	2.2	8.8	4.1
粒度 : コールターカウンター					
D : 50 (μ m)		3.0	3.2	1.8	4.7
D : 80 (μ m)		4.5	5.6	3.9	10.3
D : 97 (μ m)		6.2	7.8	7.8	21.2
窒素吸着	比表面積 (m ² /g)	103	116	192	144
水蒸気吸着	比表面積 (m ² /g)	23.8	37.6	200	59.8
	表面水酸基 密度 (個/nm ²)	2.2	3.1	9.8	4.6

[0036] In addition, measurement of a surface water acid radical consistency was based on the following approach. Measuring method of a surface water acid radical consistency [bibliography: The front face 29 (5) besides **** Hiromitsu, 362(1991)]

The five or more steam amounts of adsorption to a silica are measured at 25 degrees C with a volumetric method using a Japanese Bell full automatic steam adsorption measuring device "BELSORP18" (trade name). From the relation between adsorbate counter pressure (X=P/PO) and the amount of adsorption (V), the amount of monomolecular layer adsorption of water (Vm) is calculated with a least square method by the BET equation, and it asks.

[0037]

[Equation 1]

$$\text{BET 式 : } \frac{X}{V(1-X)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} X$$

P : maximum vapor tension C of the water in water-vapor-pressure PO:25 degree C at the time of an adsorption equilibrium : A constant V, Vm: [cm³ (S. T.P.)/g]

[0038] Specific surface area (a surface water acid radical consistency is calculated from SN2 (Japanese Bell full automatic nitrogen adsorption measuring device "BELSORP28" (trade name) use) and the amount of monomolecular layer adsorption of said water (Vm).) for which it asked by the BET equation from adsorption measurement of the nitrogen in liquid nitrogen temperature on the other hand

[0039]

[Equation 2]

$$\text{表面水酸基密度 (個/nm}^2\text{)} = 26.9 \times V_m / S_{N2}$$

[0040] Preferential grinding of the examples 1 and 2 and [examples 1 and 2 of comparison] PEFURAZOETO 20 section, the ligninsulfonic acid sodium 3 section, the fatty-acid polyoxyethylene sorbitan 1 section, the polyoxyethylene alkylphenol ether 1 section, said silica 30 section, and the clay 45 section was carried out, and the PEFURAZOETO content hydration agricultural-chemicals constituent was obtained.

[0041] Preferential grinding of the examples 3 and 4 and [examples 3 and 4 of comparison] fenitrothion 40 section, the alkyl-benzene-sodium-sulfonate 3 section, the naphthalene sulfonic-acid formalin condensate 1 section, said silica 40 section, and the clay 16 section was carried out, and the fenitrothion content hydration agricultural-chemicals constituent was obtained.

[0042] Preferential grinding of the examples 5 and 6 and [examples 5 and 6 of comparison] etofenprox 10 section, the polyoxyethylene alkylphenol ether 2 section, the naphthalene sulfonic-acid formalin condensate 2 section, said silica 20 section, and the clay 66 section was carried out, and the etofenprox content hydration agricultural-chemicals constituent was obtained.

[0043] Next, the following approach estimated the amount of flocking settling of the above hydration agricultural-chemicals constituent. A result is shown in Table 2.

A **** lump and 3 times hard water are added for 3.3g of hydration agricultural-chemicals constituents to an owner plug measuring cylinder with 100ml graduation of the amount measuring methods of flocking settling, and it considers as constant volume.

[0044] Next, after making a plug a measuring cylinder and doing a handstand violently 30 times, it puts, the volume of the sediment after 30-minute progress is measured, and it considers as the amount of flocking settling. in this case -- if the amount of flocking settling is 2ml or less -- practical use -- it is estimated that it has sufficient flocking-settling tightness.

[0045]

[Table 2]

	シリカ種類	表面水酸基密度 (個/nm ²)	農薬有効成分	凝集沈降量 (ml)
実施例 1	シリカ (1)	2.2	ペフラゾエート	1.0
実施例 2	シリカ (2)	3.0	〃	1.5
比較例 1	市販シリカ A	9.8	〃	25
比較例 2	市販シリカ B	4.6	〃	33
実施例 3	シリカ (1)	2.2	フェニトロ チオン	0.3
実施例 4	シリカ (2)	3.0	〃	0.9
比較例 3	市販シリカ A	9.8	〃	6.8
比較例 4	市販シリカ B	4.6	〃	7.1
実施例 5	シリカ (1)	2.2	エトフェン プロックス	0.8
実施例 6	シリカ (2)	3.0	〃	1.1
比較例 5	市販シリカ A	9.8	〃	7.7
比較例 6	市販シリカ B	4.6	〃	8.2

[0046] From the result of Table 2, when water is made to distribute the hydration agricultural-chemicals constituent with which the surface water acid radical consistency made the sedimentation nature silica of two or less [3.5 //nm] support an agricultural-chemicals active principle, being that by which flocking settling is controlled notably is admitted.

[0047]

[Effect of the Invention] When water is made to carry out suspension distribution, the hydration agricultural-chemicals constituent of this invention shows high distributed stability to it, and it cannot carry out flocking settling to it easily. For this reason, while excelling in the spraying workability of agricultural chemicals, there is also no

concentration fall of the agricultural-chemicals active principle in dispersion liquid, and that expected effectiveness is demonstrated effectively.